Introduction
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Nature has played and continues to play a major role in the development of and progress in organic chemistry. All life processes are essentially achieved by arrays of molecules working together in synchronisation rather than by discrete molecules acting in isolation. In order to duplicate the diversity and complexity of the life processes, there is a need to understand the factors that control aggregation of molecules into assemblies performing specific functions. Thus, the quest for replicating even remotely similar systems to that of Nature led to the development of a totally new branch of chemistry called Supramolecular Chemistry, defined as 'the chemistry concerning the structures and functions of Supermolecules formed by association resulting from the molecular interactions between two or more molecules/chemical species, i.e., chemistry beyond the concept of molecule'. This branch of chemistry, though nominally organic chemistry with respect to the species involved, has revolutionised the concept of synthesis, for it is no longer concerned with forming covalent bonds to create molecules alone, but also in harnessing noncovalent forces to create supermolecules.

Conceptually, supramolecular chemistry can be broadly classified into host-guest chemistry and self-assembly. The former involves species combining with one another in small integer ratios, comprising a host that specifically accommodates a guest, thus leading to molecular recognition. The latter describes the building up of noncovalent arrays of defined geometry from specifically engineered molecular components. Supramolecular chemistry is,
therefore, the chemistry of noncovalently bound species and noncovalent interactions play an important role in self-assembly and stabilisation of supermolecules. The forces encountered in supramolecular chemistry are electrostatic interactions, van der Waals interactions, hydrogen bonding and charge transfer interactions. Unlike covalent forces, the above mentioned forces are much weaker and are easily disrupted (a typical H-bond has $20 \text{ kJ mol}^{-1}$ energy and a lifetime of the order of $10^3$ sec). Despite their lability, many higher order structures are capable of discrete existence on the same time scale as covalent species due to the large number, and often co-operative nature, of the interactions involved, as also the high structural organisation produced through multiple binding. This organisation which is recognition directed, i.e., directed by the capacity to distinguish one spatial relationship from another, requires the presence of information that is expressed at the molecular level as two types of fundamental complementarity: steric and functional. Steric complementarity plays a vital role in reaching an optimal geometry and interface for weak interactions. Functional complimentarity refers to the reciprocal functionality with which the subunits enter into noncovalent bonding relationships. To express a preferred molecular motif on a molecular scale, a species with the right kind of functional and steric information is required which could recognise and organise into the supermolecule desired.

Ever since the report of the discovery of the first synthetic ionophores by C. J. Pedersen in 1967, and more so since the awarding of the Nobel prize to C. J. Pedersen, D. J. Cram and J.-M. Lehn, the pioneers of this field, there has been an impetus to synthesise more and more novel structures with fascinating micro and macroscopic architectures endowed with novel functions. A concise
description of supramolecular systems that exemplify the above mentioned noncovalent interactions is therefore in order.

Multidentate macrocyclic compounds with heteroatoms, such as O, N, S, P and Se, having the ability to incorporate specific cations into their cavities were amongst the first to be synthesised. They are referred to by a general term, coronand. A multitude of them have been synthesised and categorised variously. The oxygen bearing macrocycles are called crown ethers, sulfur containing ones, thiacrown ethers and nitrogen bearing ones, azacrowns. Their acyclic counterparts, termed as podands, show very little selectivity, whereas their bicyclic counterparts with bridgeheads, called cryptands, display tetrahedral recognition. The most striking feature of these compounds is their selective complexation ability to bind the cationic portion of alkali, alkaline earth, transition metal, ammonium and guanidinium salts, incorporating them as guests into the cavity of the crown ring (host) through ion-dipole interactions (Fig. 1).
Selectivity in binding depends upon the size of the cavity of the host and diameter of the guest; the number of donor (hetero) atoms in the crown and topological effect; hardness of the host and the guest as well as the charge on the cation. These crowns and cryptands have been found to have a variety of analytical applications like separation, extraction, chromatography and electrophoresis of elements of the first and the second group. They have also been found to be excellent phase transfer catalysts.

The scenario underwent a complete transformation with the advent of bis crowns and multiloop crowns. More than one cation of same or different type could now be bound to the same host. This inspired the design and synthesis of novel hosts (eg. 4, Fig. 2) that could bind cations and anions simultaneously. A tighter binding of the guest could be achieved by a series of armed crown ethers or lariat ethers, wherein the co-operation between the ring and the side arm seals the guest tightly into the cavity. A typical example, azacrown ether 5 with side arms containing acetic acid moieties, encapsulates cations of lanthanide series of elements with an enhanced binding. Such systems are gaining popularity due to their applications in magnetic resonance imaging.

![DITOPIC BINDER (4)](image1)

![5](image2)

**Figure 2**
In all the above cases, conformational changes occur in the host during the complexation process, i.e., self organisation of the host takes place, which requires energy. In order to overcome this, Cram designed host molecules with rigid cavities in which conformational changes do not take place during the process of complexation. Thus, the host is now said to be preorganised to show more rigorous binding. The cavitands and spherands (6, Fig. 3) fall into this category. Among the preorganised hosts gaining prevalence of late are calixarenes, that also bind cations, selectivity being a function of cavity size and nature of binding groups (7, Fig. 3).

Designing receptors for neutral molecules is still relatively a more challenging and less explored domain. Recently Hamilton reported a highly
stable complex of the host 8 (Fig. 4) and a neutral guest by means of a designed network of hydrogen bonds.

Very large, rigid cavities required to bind big molecules are very often difficult to construct. Moreover, it is observed that biomolecules like enzymes rarely have cavities that surround the substrate completely. This perception led to the designing of non-macrocyclic hosts with preorganised aromatic clefts, called molecular tweezers, that contain two aromatic chromophores separated by a covalently linked spacer. They bind aromatic guests by forming a π-stacked, sandwich complex (9, Fig. 4).

Cyclophane type macrocycles containing aromatic units have a hydrophobic cavity of definite shape and dimensions. Molecular recognition study of a water soluble cyclophane host 10 (Fig. 5) synthesised by Lehn
reveals that in aqueous medium the binding forces are both electrostatic and hydrophobic. The host 10 was found to bind to a variety of quaternary ammonium salts and acetylcholine.

![Diagram of molecular structures](image)

**Figure 5**

Cation-K and \( \pi-\pi \)-stacking interactions have been exploited in designing hosts for aromatic molecules (11, Fig. 5). The K-stacking and charge transfer interactions between K-electron rich and K-electron deficient systems function as templates for the one pot self assembly of interlocked rings or catenanes as well as beads on threads or rotaxanes (Fig. 6).
Figure 6

SELF-ASSEMBLY OF ROTAXANE
The knowledge gained by understanding the role played by noncovalent interactions in the self assembling processes of these simple artificial systems has led not only to a better understanding of physical organisation in biological systems, but has also inspired building of simple molecular devices, molecular machines (Fig. 7)\textsuperscript{19} and molecular switches (Fig. 8).

Figure 7  

![A Molecular Brake](image)

Figure 8  

![An Organic Switch](image)
From the brief description given above, it is clear that remarkable progress has been made in understanding host-guest interactions at the molecular level. However, there still exists a vast scope for further understanding the noncovalent interactions that hold the supramolecular structures together. An in-depth understanding of the structure-information-function relationship alone can lead to the development of supramolecular devices which can rival the ones that already exist in Nature. Central to this mission is the development of novel and simple chemical systems that can organise on their own due to their inherent recognition capabilities. In this context, we have undertaken the design, synthesis and study of some oxygen macrocycles and podands, each with a special kind of binding property involving different types of noncovalent interactions.

This thesis, dealing with some aspects of supramolecular chemistry is divided into three chapters. Chapter 1 is concerned with supermolecules assembled by \( \pi \)-stacking and charge transfer interactions involving a new naphthalene based macrocycle and suitable guests having \( \pi \)-stacking capabilities. Chapter 2 presents the synthesis of rigid molecular hosts based on Troger's bases and their cation binding abilities. Encapsulation of podands by hydrophobic cavities of cyclodextrins and the influence of this on their photophysical properties is discussed in chapter 3.
References:


